

# Analysis of silicon, phosphorus and sulfur in 20% methanol using the Agilent 8800 Triple Quadrupole ICP-MS

## Application note

Semiconductor analysis; metallomics; energy & fuels

### Author

Emmett Soffey, Bert Woods and Steve Wilbur

Agilent Technologies  
Bellevue, WA, USA

|       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|
| 13 Al | 14 Si | 15 P  | 16 S  | 17 Cl | 18 Ar |
| 31 Ga | 32 Ge | 33 As | 34 Se | 35 Br | 36 Kr |

## Introduction

Analysis of trace elements in organic solvents presents a number of challenges to ICP-MS, many of which have been overcome to varying degrees on Agilent's 7700 Series quadrupole ICP-MS systems, using technological advances including a Peltier-cooled spray chamber, fast variable-frequency impedance matching solid state RF generator and octopole-based collision/reaction cell (ORS<sup>3</sup>). However, even with these advances, several elements remain challenging in organic solvents, particularly silicon, phosphorus and sulfur. All three elements are subject to intense interferences from polyatomic ions based on carbon, nitrogen and oxygen, which are difficult to completely remove using conventional ICP-MS. Examples include CO, COH, N<sub>2</sub> and NO on silicon 28, 29 and 30, COH, NOH, N<sub>2</sub>H, NO and CO on phosphorus 31, and O<sub>2</sub>, NO, NOH and NOH<sub>2</sub> on sulfur 32 and 34. Additionally, phosphorus and sulfur have high first ionization potentials (IP) of 10.5 eV and 10.4 eV respectively, resulting in relatively poor sensitivity compared to more typical elements whose IPs are in the range of ~6-8 eV.



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Silicon, phosphorus and sulfur are all important analytes in organic solvents used in the semiconductor manufacturing industry, which is largely silicon based. Phosphorus is a common dopant in wafer manufacturing, and sulfur hexafluoride gas is used as an etchant. Contamination of the wafer by trace elements including P and S, even at ultratrace levels, can render a chip unusable, so the control of these elements in the water, acids and organic solvents that come into contact with the wafer surface is a critical requirement in semiconductor manufacturing.

Sulfur and phosphorus are important trace analytes in the organic solvents used in many other applications outside the semiconductor industry, including hydrocarbon processing, and particularly in life sciences research. Because ICP-MS is an elemental detector and therefore gives the same response for a given sulfur concentration regardless of the compound in which it occurs, ICP-MS analysis of sulfur permits the quantification of sulfur-containing proteins and peptides without the requirement for compound-specific calibration standards. This technique is called compound independent calibration (CIC) and is a major benefit of ICP-MS for life science research. Other developing applications for ICP-MS include the quantification of nucleotides (DNA and RNA) based on their phosphorus content. Additionally, regulation of enzyme activity through phosphorylation is an important area of biological research that requires highly sensitive and specific phosphorus determination. Speciation analysis of biomolecules typically involves separation

by HPLC, followed by analysis using ICP-MS. Since LC mobile phases commonly contain methanol, the ability to determine trace Si, P and S in methanol was tested using the new Agilent 8800 Triple Quadrupole ICP-MS.

## Experimental

Ultra pure methanol was diluted 1:5 with ultrapure water and spiked with silicon, phosphorus and sulfur at 1, 5, 10 and 50 ppb. These standards were measured using the Agilent 8800 ICP-Triple Quad in several operational modes in order to evaluate the optimum conditions for the simultaneous analysis of all three analytes.

The 8800 combines two quadrupole mass filters, Q1 before and Q2 after the Octopole Reaction System (ORS<sup>3</sup>) cell (Figure 1), in a tandem mass spectrometer (MS/MS) configuration. The normal mode of operation of the 8800 is MS/MS mode, where the first quadrupole works as a unit mass filter, restricting the ions entering the ORS<sup>3</sup> cell to a single mass to charge ratio ( $m/z$ ) at any given time. In this way, ions entering the collision reaction cell are precisely controlled, resulting in the ability to exactly control the reaction chemistry occurring in the cell, even if the sample composition changes. This is in contrast to conventional quadrupole reaction cell instruments, where there is no control over the ions that enter the cell and undergo reactions with the cell gas. MS/MS supports both direct, 'on-mass' measurement, and indirect or 'mass shift' mode. On-mass measurement is used when the analyte is unreactive and is measured at its natural mass, while

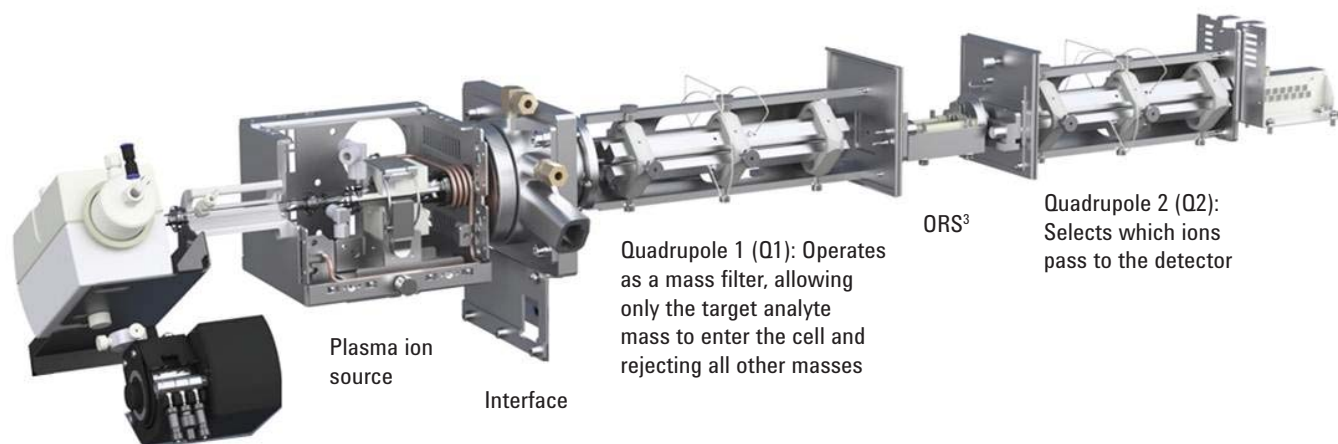


Figure 1. Schematic of the Agilent 8800 Triple Quadrupole ICP-MS

the interferences are reactive and are removed. Mass-shift mode is used when the analyte is reactive and the analyte ions are moved away from the interfering ion overlaps at the original  $m/z$  through the formation of an analyte reaction product ion at a new mass. The 8800 can also be operated in single quad mode, where the first quadrupole acts as a low mass cutoff filter, essentially transmitting all ions above a specified mass to the ORS, and the second quadrupole is used for mass analysis. In single quad mode, the 8800 operates in a similar way to a conventional quadrupole ICP-MS. In this work, hydrogen and oxygen reaction gases were evaluated, with  $H_2$  cell gas used in both single quad and MS/MS modes. In addition, helium collision gas was investigated in both single quad and MS/MS mode to determine the effects of using MS/MS mode with a non-reactive cell gas.

The instrument conditions used are outlined in Table 1, which includes the five analysis modes evaluated. Two single quad modes were tested, using He or  $H_2$  in the cell, to simulate the capability of a conventional quadrupole ICP-MS. In addition, three MS/MS modes were tested using  $H_2$ , He or  $O_2$  as the cell gas. It is notable that plasma and ion optic (extraction lens settings) conditions were identical for all five modes, making it fast and simple to switch between the various modes.

**Table 1.** Agilent 8800 ICP-MS acquisition conditions tested, including five operational modes: two single quad modes, and three MS/MS modes. 'Q2 offset mass' is the mass difference between Q1 and Q2 to measure analyte reaction product ions.

| Tune                           | He mode     | $H_2$ mode  | $H_2$ MS/MS | He MS/MS | $O_2$ MS/MS |
|--------------------------------|-------------|-------------|-------------|----------|-------------|
| Scan mode                      | Single quad | Single quad | MS/MS       | MS/MS    | MS/MS       |
| RF power (W)                   | 1550        |             |             |          |             |
| Sample depth (mm)              | 8           |             |             |          |             |
| Carrier gas flow rate (mL/min) | 1.05        |             |             |          |             |
| Ext 1 (V)                      | 0           |             |             |          |             |
| Ext 2 (V)                      | -190        |             |             |          |             |
| Cell gas/flow rate (mL/min)    | He / 5      | $H_2$ / 7   | $H_2$ / 7   | He / 5   | $O_2$ / 0.4 |
| KED (V)                        | 5           | 0           | 0           | 5        | -7          |
| Q2 offset mass (amu)           | N/A         | N/A         | 0, 2, 3     | 0        | 0, 16, 32   |

## Results and discussion

The background equivalent concentration (BEC) and detection limit (DL) results are summarized in Tables 2–4, for silicon, phosphorus and sulfur respectively, for all five analysis modes tested. Single quad and optimum MS/MS results are in bold type for comparison. The two masses listed under  $m/z$  monitored in MS/MS mode are the settings for Q1 and Q2 respectively. For example, Table 2 shows silicon monitored in  $O_2$  MS/MS mode using masses 28 and 44. With Q1 set to  $m/z$  28, only silicon 28 and any on-mass interferences are allowed to enter the ORS<sup>3</sup> cell. The silicon 28 in the cell reacts with the oxygen cell gas to form the product ion  $^{16}Si^{16}O^+$ , and Q2 is set to measure this reaction product ion at Q1 + 16 ( $m/z = 44$ ), ensuring that only the +  $^{16}O$  reaction transition is measured. This specific mass-shift monitoring capability is unique to MS/MS mode and means that the isotopic pattern of the analyte is maintained, since possible isotopic overlaps such as  $^{28}Si^{18}O^+$  on  $^{30}Si^{16}O^+$  cannot occur. The polyatomic ions that interfered with direct measurement of Si at  $m/z = 28$  do not react with oxygen to form product ions at  $m/z = 44$ , and so are eliminated by Q2.

**Table 2.** Detection limits (DLs,  $3\sigma$ ) and background equivalent concentrations (BECs) for silicon. Silicon was not measurable at the spiked concentrations in helium mode.

| Mode                       | <i>m/z</i> monitored | BEC (ppb)    | DL (ppb)    |
|----------------------------|----------------------|--------------|-------------|
| H <sub>2</sub> single quad | <b>28</b>            | <b>25.46</b> | <b>0.12</b> |
| H <sub>2</sub> MS/MS       | <b>28/28</b>         | <b>2.17</b>  | <b>0.03</b> |
| O <sub>2</sub> MS/MS       | 28/44                | 85.54        | 28.21       |
| O <sub>2</sub> MS/MS       | 30/46                | 99.09        | 21.26       |

**Table 3.** Detection limits (DLs,  $3\sigma$ ) and background equivalent concentrations (BECs) for phosphorus. Phosphorus was not measurable at the spiked concentrations in hydrogen single quad mode.

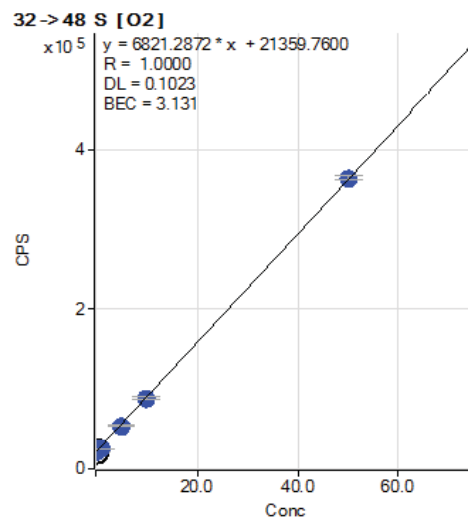
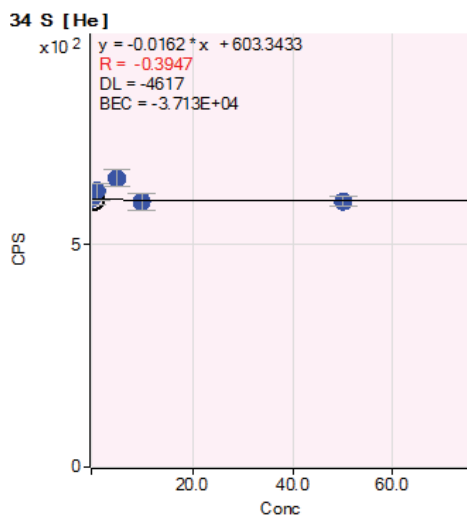
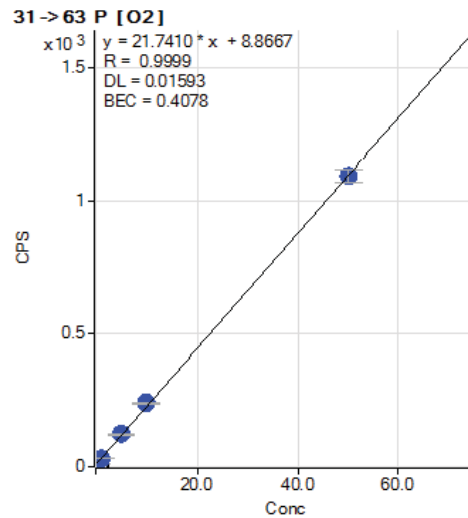
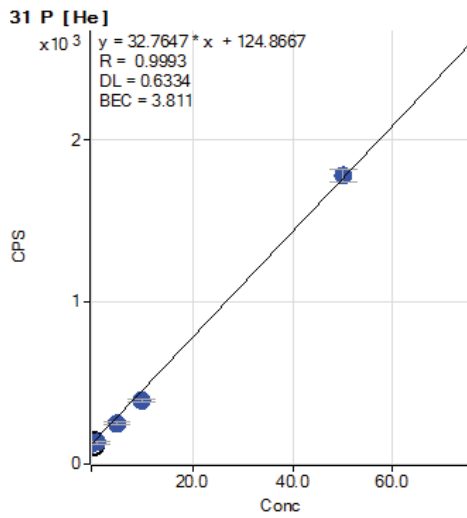
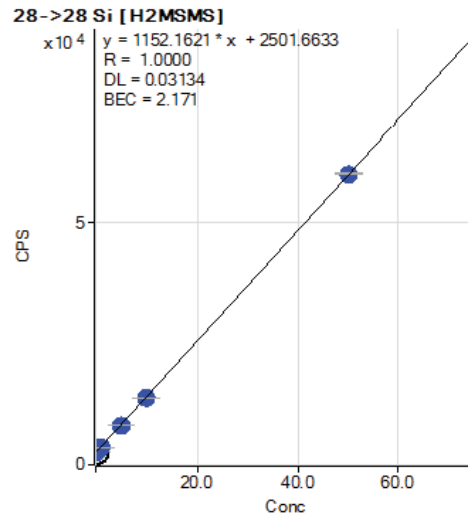
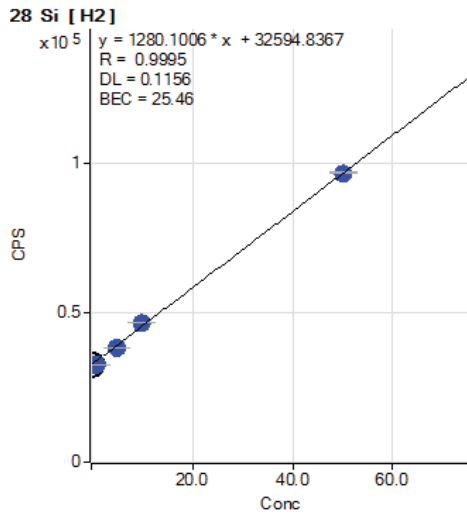
| Mode                 | <i>m/z</i> monitored | BEC (ppb)   | DL (ppb)    |
|----------------------|----------------------|-------------|-------------|
| He single quad       | <b>31</b>            | <b>3.81</b> | <b>0.63</b> |
| He MS/MS             | 31/31                | 2.99        | 0.72        |
| H <sub>2</sub> MS/MS | 31/33                | 0.56        | 0.07        |
| H <sub>2</sub> MS/MS | 31/34                | 0.58        | 0.67        |
| O <sub>2</sub> MS/MS | 31/47                | 0.40        | 0.05        |
| O <sub>2</sub> MS/MS | <b>31/63</b>         | <b>0.41</b> | <b>0.02</b> |

**Table 4.** Detection limits (DLs,  $3\sigma$ ) and background equivalent concentrations (BECs) for sulfur. Sulfur was not measurable at the spiked concentrations in helium or hydrogen mode.

| Mode                 | <i>m/z</i> monitored | BEC (ppb)   | DL (ppb)    |
|----------------------|----------------------|-------------|-------------|
| O <sub>2</sub> MS/MS | 34/34                | 51.17       | 4.37        |
| O <sub>2</sub> MS/MS | <b>32/48</b>         | <b>3.13</b> | <b>0.10</b> |
| O <sub>2</sub> MS/MS | 34/50                | 3.11        | 0.20        |

The sample calibration plots in Figure 2 are displayed in pairs showing the results using single quad mode with a typical cell gas, compared with MS/MS mode using the optimum conditions.

It can be seen that in all cases, the use of MS/MS mode significantly improves both the BEC and instrument detection limit when compared with single quad mode. The most notable improvement was for sulfur (Figure 2, bottom), which cannot be measured at the spiked concentrations (1, 5, 10, 50 ppb) in single quad He mode due to the intense polyatomic background resulting from the methanol:water matrix. For this reason, trace level analysis of sulfur using the 7500 or 7700 Series quadrupole ICP-MS has typically been performed using Xe reaction mode, which gives the best reduction of the O<sub>2</sub> interference. However, Xe is very expensive and Xe reaction mode is not ideal for other elements, due to severe loss of sensitivity for low mass ions due to scattering from the large Xe molecules in the cell. This has made the simultaneous analysis of sulfur with other analytes difficult in chromatographic applications.



**Figure 2.** Example calibration curves for silicon, phosphorus, and sulfur showing single quad results (left) compared with MS/MS results (right). Sulfur is not measurable at the spiked concentrations in methanol in single quad mode due to the intense polyatomic interference (left). All concentration units are ug/L (ppb).

## Conclusions

The Agilent 8800 ICP-Triple Quad provides significantly enhanced sensitivity and interference reduction for the challenging elements; silicon, phosphorus and sulfur in organic matrices when compared with conventional quadrupole ICP-MS systems. The 8800 achieves this superior performance by utilizing MS/MS mode, where the first quadrupole eliminates all but the analyte mass and any interfering ions at the same  $m/z$ . By rejecting all non-target masses, the reaction chemistry in the cell is controlled and consistent, resulting in highly efficient and predictable interference removal. Q1 also rejects any off-mass ions that might overlap the analyte product ions created in the cell, thereby greatly improving the accuracy and reliability of reaction gas modes that use mass-shift. In addition, the higher sensitivity and lower background of the 8800 provide improved detection limits compared with quadrupole ICP-MS, even when operated in single quad mode.

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